



Battery500 Consortium

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2017 DOE Vehicle Technologies Program Review
June 8, 2017

Project ID
ES317

Overview

Timeline

- Start date: September 2016
- End date: September 2021
- Percent complete: 10%

Budget

- Total project funding: \$50M
 - DOE share 100%
- Funding received in FY 2016: \$10M
- Funding for FY 2017: \$10M



Barriers

- Barriers addressed
 - Increasing energy density of advanced lithium (Li) metal batteries beyond what can be achieved in today's Li-ion batteries is a grand scientific and technological challenge.

Partners

- Project lead: Pacific Northwest National Laboratory
- Partners: Binghamton University, Brookhaven National Laboratory, Idaho National Laboratory, SLAC, Stanford University, University of California San Diego, University of Texas at Austin, University of Washington

Relevance/Objectives

- The Battery500 Consortium aims to triple the specific energy (to 500 Wh/kg) relative to today's battery technology and achieve 1,000 charge/discharge cycles.
- The consortium aims to overcome the fundamental scientific barriers to extract the maximum capacity in electrode materials for next generation Li batteries.
- The consortium leverages advances in electrode materials and battery chemistries supported by DOE.
- Advance in understanding Li metal deposition and failure mode in high capacity electrode materials will have impact on current battery technologies.

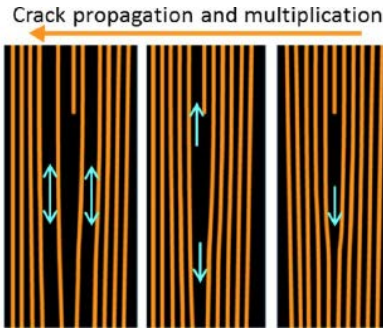
Milestones

Date	Milestones	Status
December 2016	Complete the establishment of baseline cathode materials, anode materials, electrolytes and cell architecture. Establish and implement project plans for all PIs and institutions.	Completed
March 2017	Complete the preliminary testing of electrode materials with controlled architectures. Complete the first synthesis of high Ni NMC material, with a specific capacity of 200 mAh/g, and bench mark with NMC622 materials from other groups.	Completed
June 2017	Develop electrolyte formulation for Li deposition with the stable oxidation voltage over 4.3 V and over 98% Coulomb efficiency.	On track
September 2017	Complete the construction of 1 Ah pouch cell with 300 Wh/kg specific energy, and over 50 cycles and continuing. Complete the preliminary testing protocol.	On track

Approach

- Develop commercially viable Li battery technologies with a cell level specific energy of 500 Wh/kg through innovative electrode and cell designs that enable utilization of maximum capacity of advanced electrode materials.
- The program is organized around three keystone projects: (1) Materials and Interfaces, (2) Electrode Architecture, and (3) Cell Design and Integration.
- Utilize a Li metal anode combined with a compatible electrolyte system, and two cathodes, a nickel-rich NMC ($\text{LiNi}_x\text{M}_{1-x}\text{O}_2$, $\text{M} = \text{Mn or Co and } x > 0.7$) and sulfur.
- Design novel electrode and cell architectures will allow 50% of the theoretical capacity to be attained at the cell level in order to meet the 500 Wh/kg goal.
- Integrate the three keystone projects, and the multi-institute capabilities in battery materials and chemistry, electrode architecture, cell design and fabrication, and advanced diagnosis to optimize the materials performance in realistic cell architectures.
- Seedling project proposals are in process.

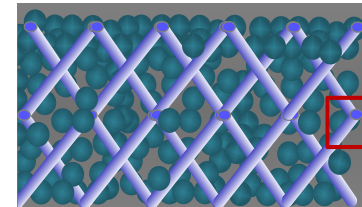
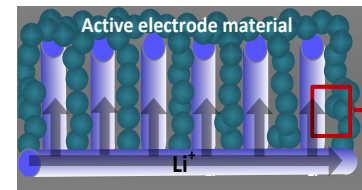
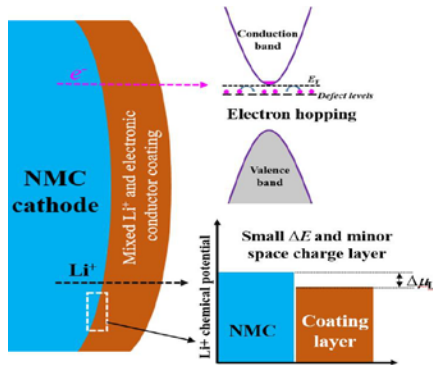
Multiscale approaches to develop thick cathode architectures



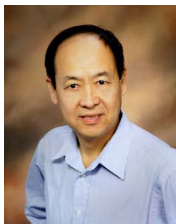
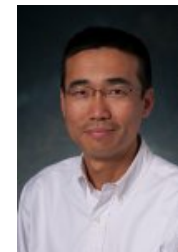
Understanding and controlling of degradation on atomic scale



Controlling of synthesis, particle morphologies and interfacial chemistry

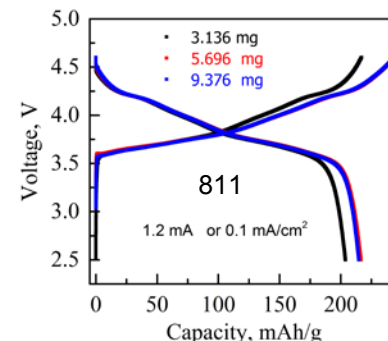
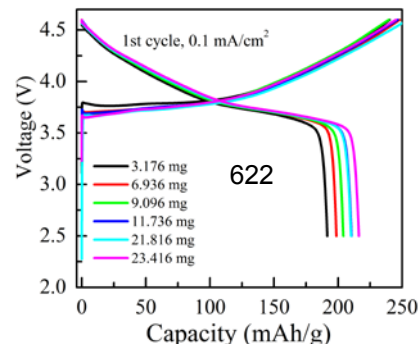
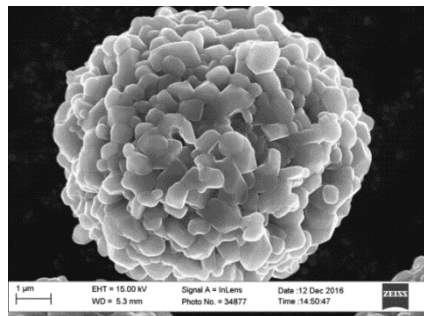
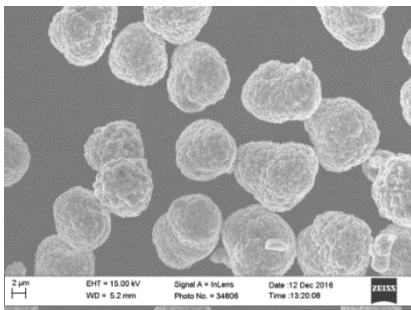


Thick electrode architecture to maximize cathode utilization



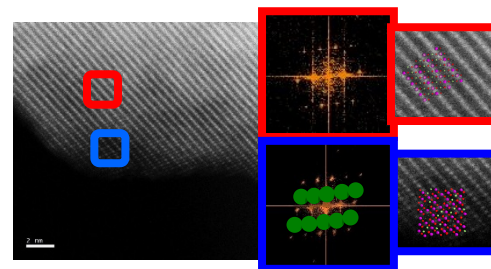
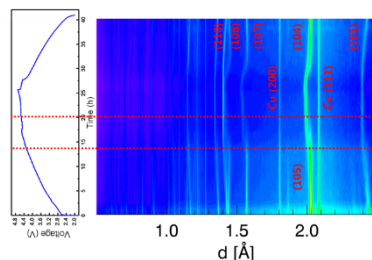
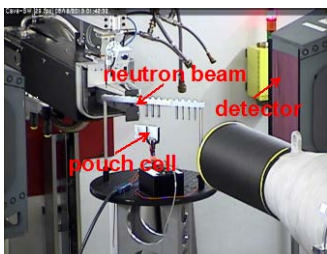
Technical Accomplishments

Investigation of baseline high Ni NMC cathode materials



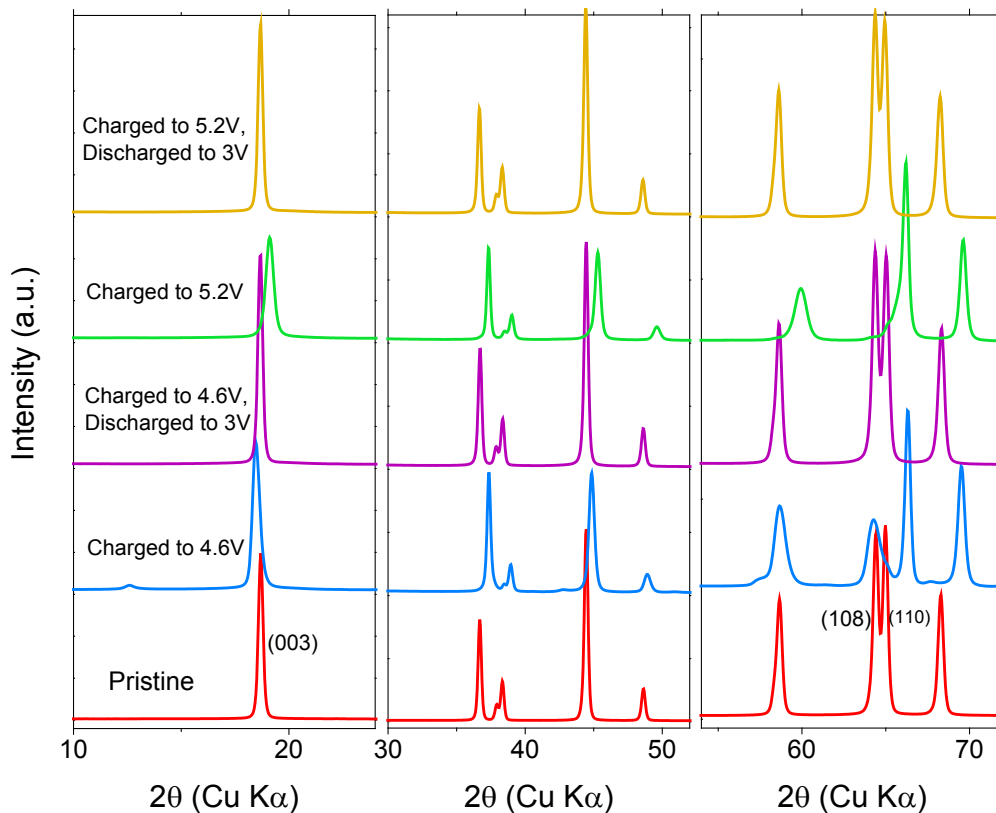
Baseline materials were obtained from commercial suppliers.

- Stable 160-180 mAh/g capacity achieved when charging limited to 4.2-4.3 V.
- 4.5 V charging leads to capacities exceeding 220 mAh/g: Capacity fading increases with increase of charging voltage.
- Materials with high Ni content will be prepared and studied.
- Explore the bulk structural changes of NMC622 up to 4.8 V and identify the degradation due to strain, defects evolution and oxygen loss.

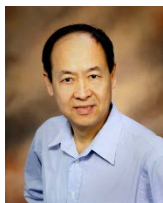


Technical Accomplishments

Ex situ XRD results of NMC622



1. After charged to 4.6V (blue), the (003) peak shifts to lower 2θ angles indicating the “c” axis expansion and the (10/0) peak shows obvious broadening, indicating disorder in the c direction. At the same time, (110) peak shifts to higher 2θ angles, indicating “a” axis contraction.
2. After charged to 4.6V and then discharged to 3V (purple), the (003), (110) and all peaks shift back to their original positions.
3. After charged to 5.2V (green), (108) peak and (110) peak merged into one peak.
4. When the cell is discharged to 3V (brown), all peaks almost fully recovered to their original positions.

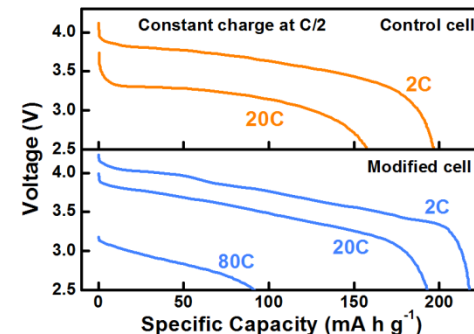
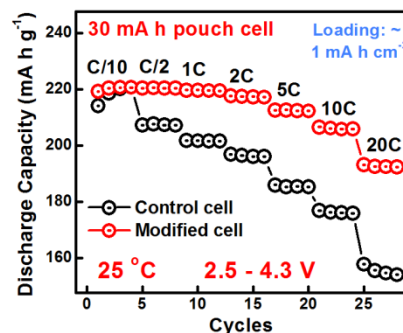
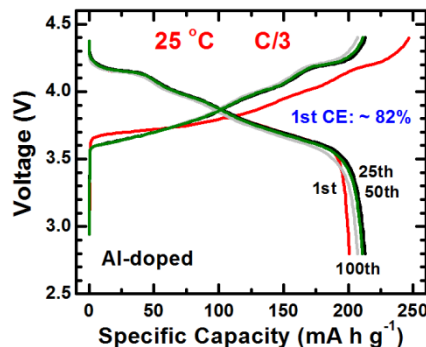
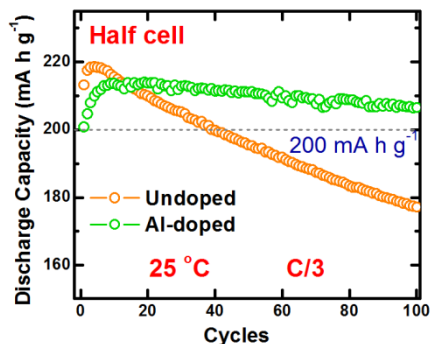
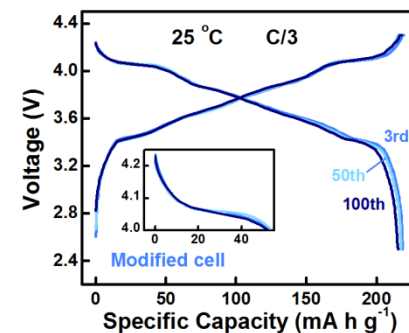
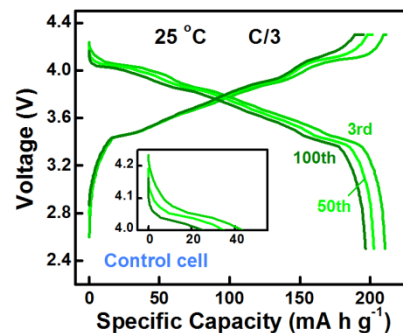
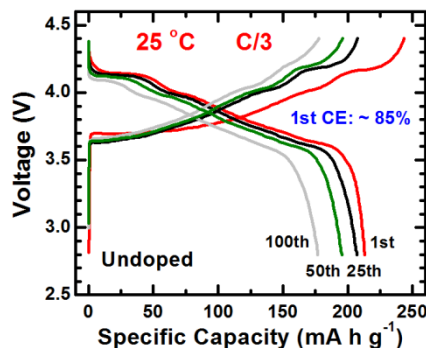
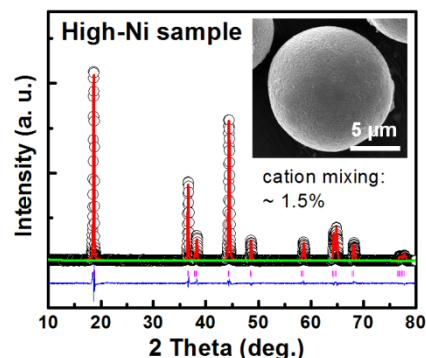


The limited reversibility of NMC622 material at high voltage is also confirmed by careful structural characterization.

Technical Accomplishments

High Ni layered oxide cathodes

Characterization and Li metal cells



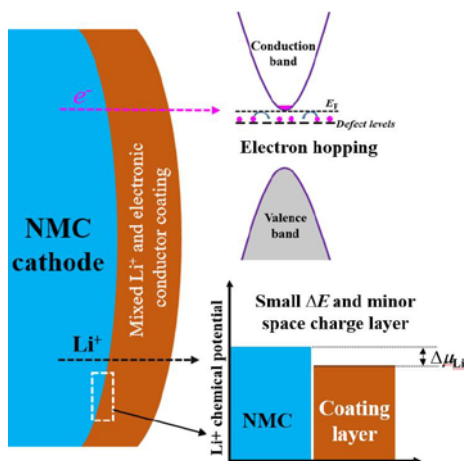
- Al-doped cathodes with 94% Ni exhibit > 200 mAh/g with superior cyclability compared to the undoped sample due to surface and bulk stabilization

- Stabilized full cells with 94% Ni cathodes exhibit ~ 220 mAh/g with superior cyclability, rate capability, and power density compared to the control cell.



Technical Accomplishments

Surface coating of NMC622 with mixed conductors

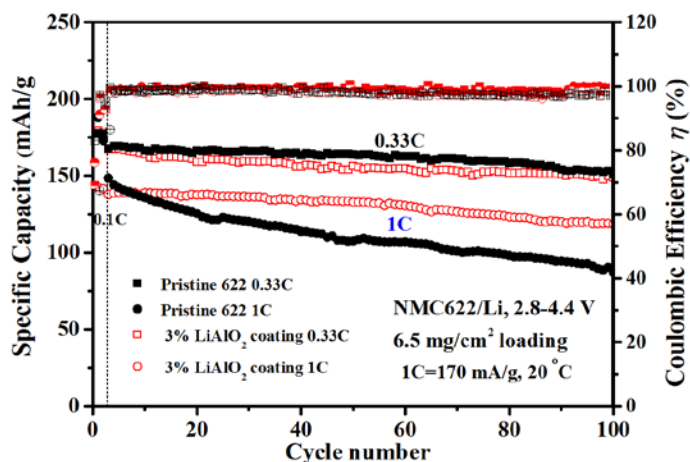


A mixed electronic and ionic conductor surface coating for high-Ni NMC622: improve the cycling performance while maintaining good rate capability:

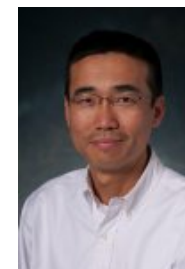
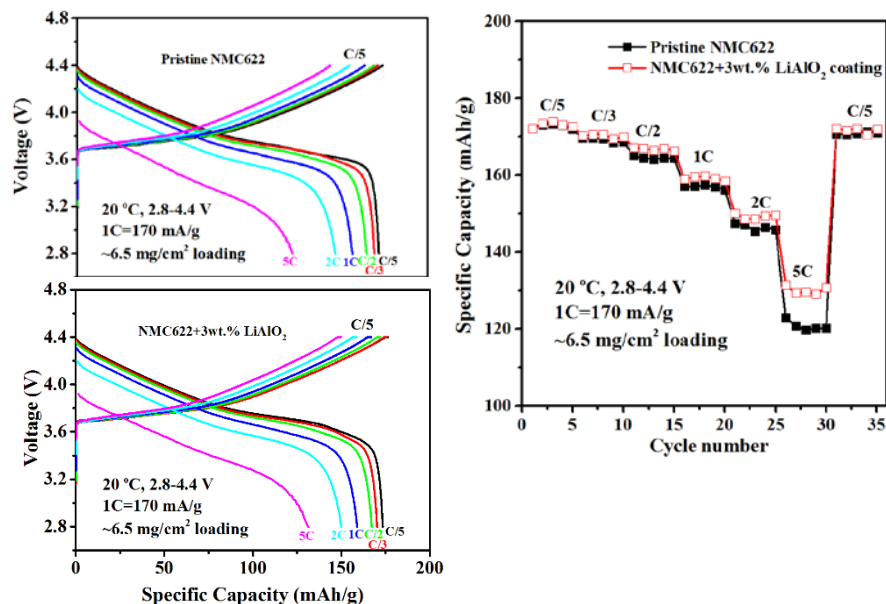
- ❑ Superior electrochemical stability with electrolytes at high V
- ❑ Fast interfacial Li⁺ transport: small chemical potential difference
- ❑ Fast electron transport: high density shallow impurity levels

NMC622: Surface coating with LiAlO₂

Superior cycling performance



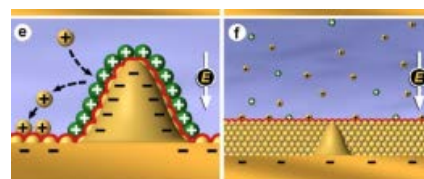
Superior rate performance



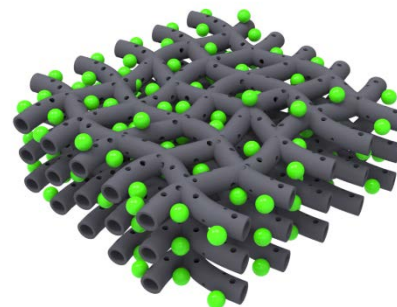
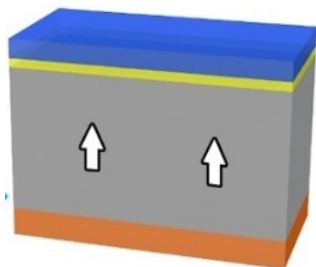
Multi-disciplinary approaches for Li metal

Interfacial wetting

Nucleation and deposition

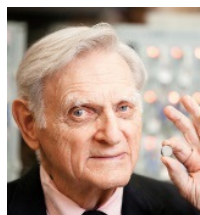


Legend:
● Li^+ ion
● Non-lithium cation
▲ Lithium tip
▲ Protuberant tip
■ Electrolyte
■ SEI Layer
■ Lithium metal



Solid electrolyte

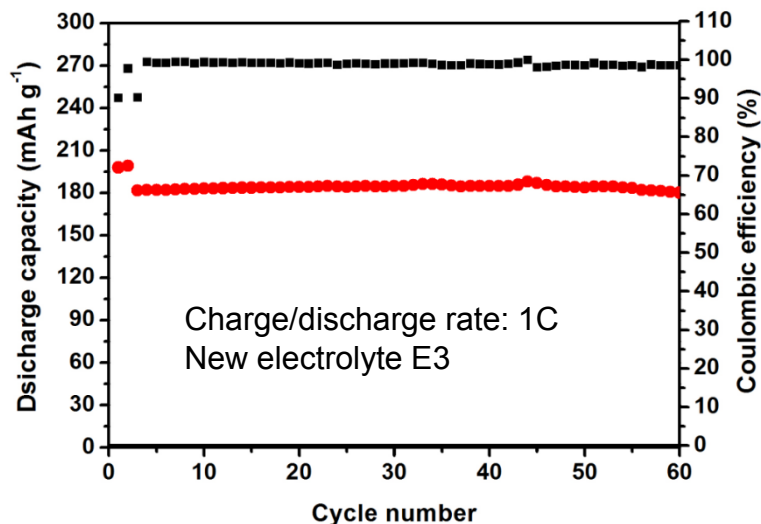
Lithium architecture



Technical Accomplishments

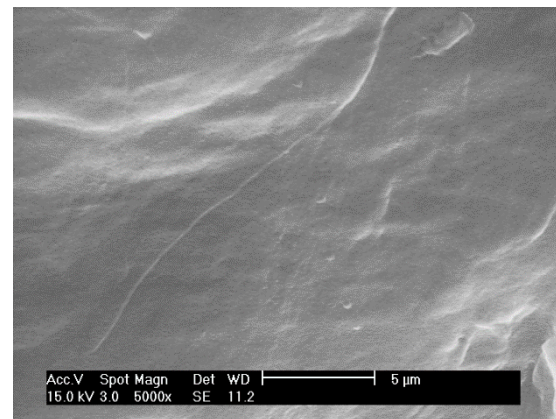
New electrolyte and Artificial SEI

Cycling performance of new electrolyte



- Li||NMC622 cells, NMC622 with 1.56 mAh/cm^2
- Voltage cutoff range: 2.8 ~ 4.4 V
- Electrolyte amount in each coin cell: $75 \mu\text{L}$
- ✓ So far the new electrolyte E3 shows good compatibility and stability with Li metal anode and NMC622 cathode as the control electrolyte does.

Synthetic SEI



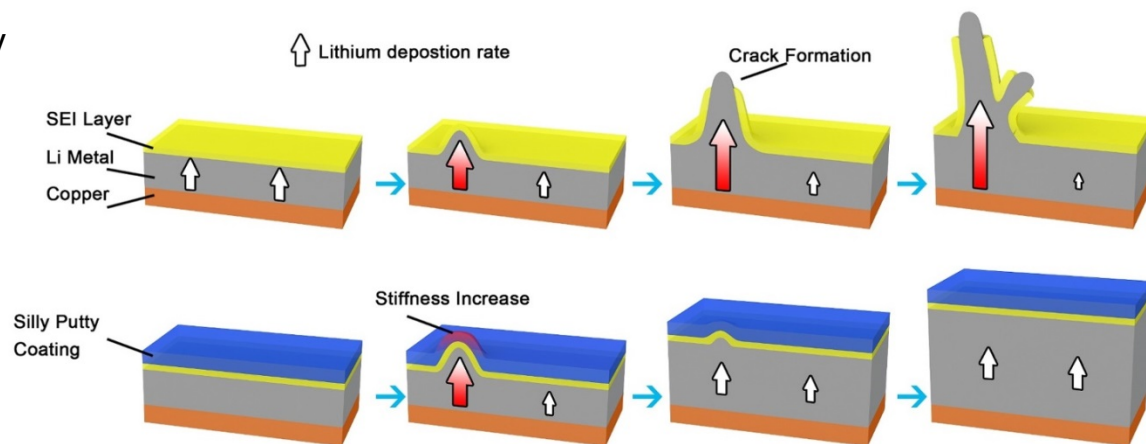
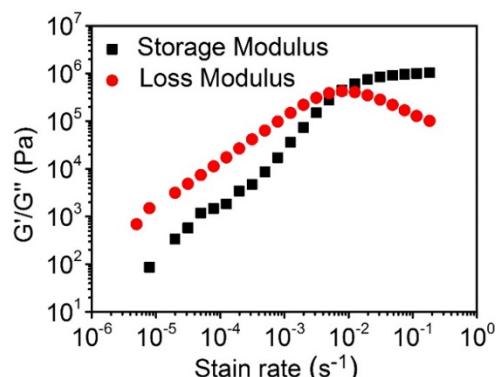
- Cross-section SEM of cycled lithium after 300 cycles at 3 mA/cm^2 (1Crate).
- ✓ Crystalline methyl lithium carbonate formed in-situ through a solution chemical process to form a robust coating on Li.

Technical Accomplishments

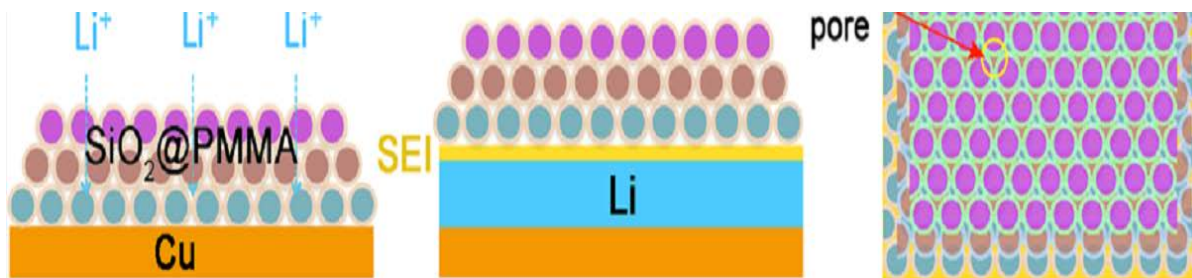
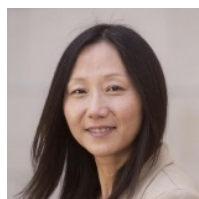
Interfacial protective layers for lithium metal anodes

Li Metal Anodes with an Adaptive “Solid-Liquid” Interfacial Protective Layer

“Solid-Liquid” property of Silly Putty

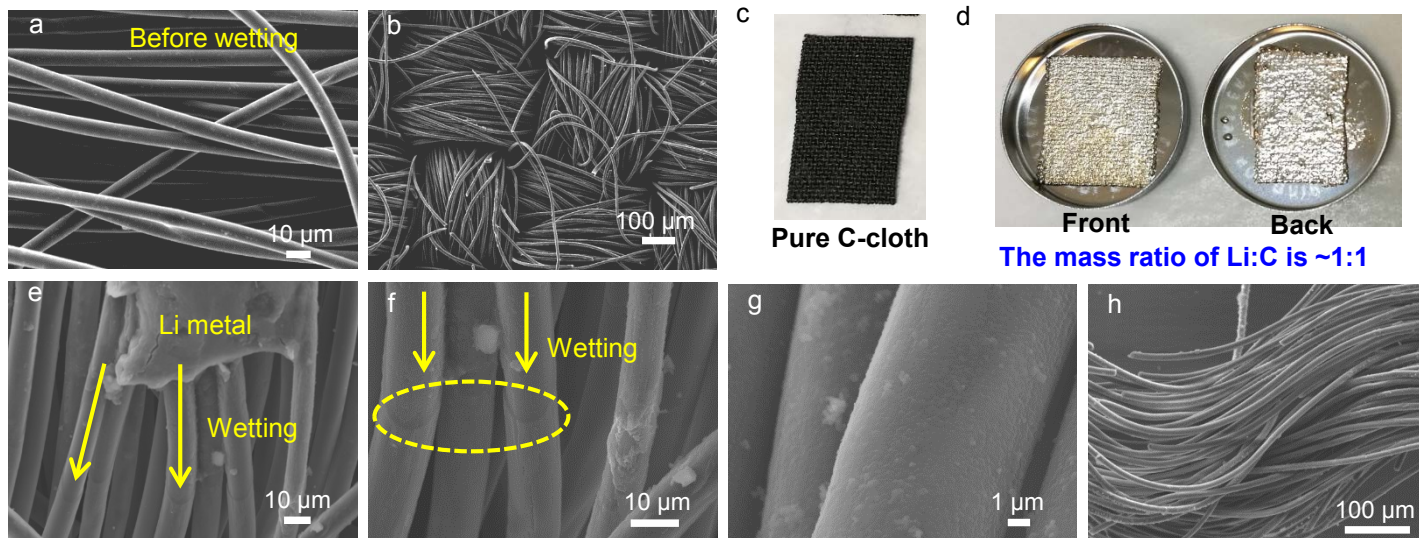


Core-Shell Nanoparticle Coating as an Interfacial Layer for Dendrite Free Li Metal Anodes

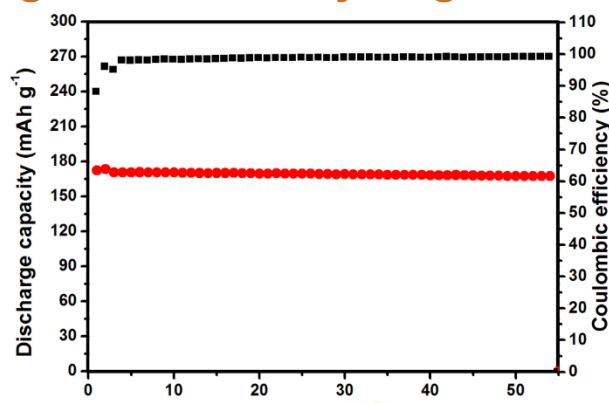
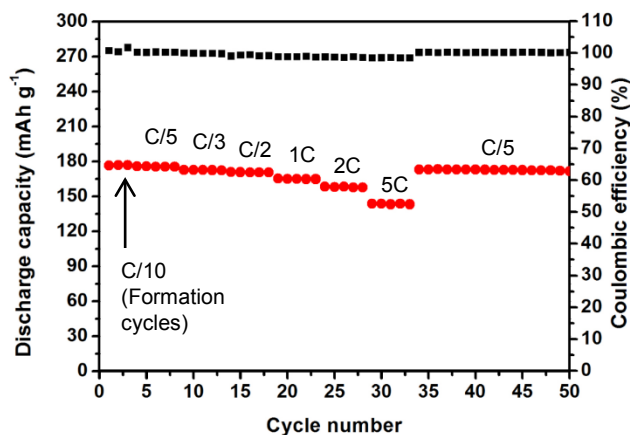


Technical Accomplishments

3D structured Li/carbon cloth composite anode and cell performance with NMC622 cathode



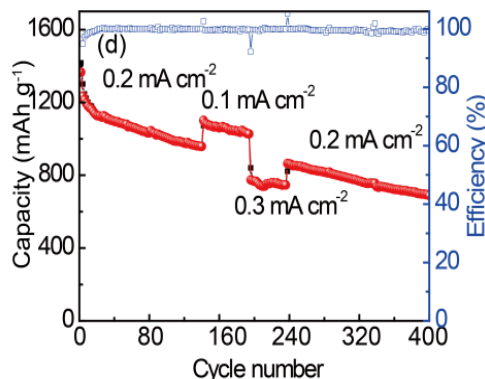
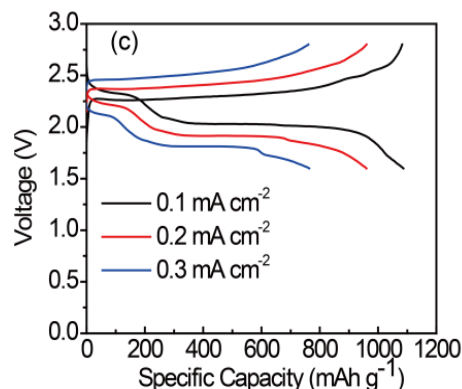
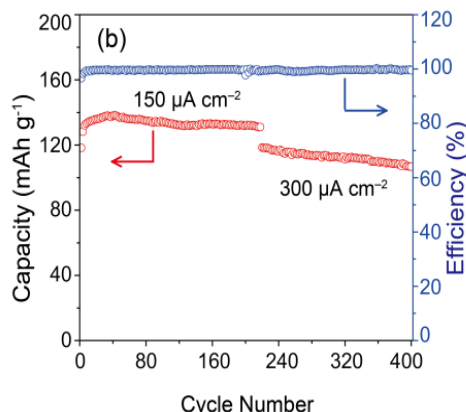
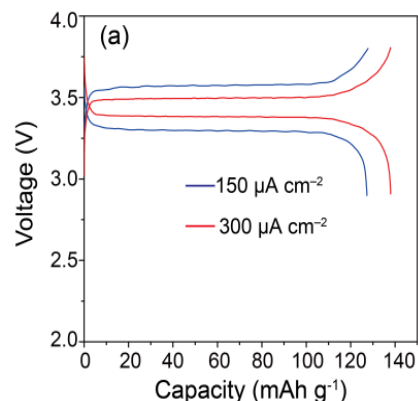
3D structured Li shows good rate and cycling stability in Li metal cells



- Li/C-cloth||NMC622
- Anode: Li/C-cloth (Li:C= 1:1 wt.)
- Cathode: NMC622, 1.56 mAh/cm²
- Electrolyte: Control electrolyte, 75 μL
- Voltage range: 2.8-4.3 V

Technical Accomplishments

Solid electrolyte $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Hf}_{1/4}\text{Ta}_{3/4}\text{O}_3$ (LSHT) with good stability for Li-ion batteries



(a) Charge and discharge voltage profiles of all-solid-state Li|LSHT|LiFePO₄ at 150 and 300 $\mu\text{A}/\text{cm}^2$.

(b) Capacity retention and cycling efficiency of the Li||LiFePO₄ cells.

(c) Charge and discharge voltage profiles of a Li-S battery with LSHT at different current densities.

(d) Capacity retention and cycling efficiency of the Li-S battery.



- ❑ Perovskite LSHT has a Li-ion conductivity of $3.8 \times 10^{-4} \text{ S/cm}$ at 25 °C;
- ❑ LSHT is stable with organic electrolytes and water with pH from 1 to 14;
- ❑ All-solid-state Li||LiFePO₄ has a long cycle life and a high Coulombic efficiency of 99.9 %;
- ❑ LSHT is stable in a Li-S battery and can block the polysulfide shuttle.



Technical Accomplishments

Evaluation and validation methods



Enhanced comparison, validation and identification of technology gaps

- Enables comparison, model verification, on-going and future data analysis/mining
- Standard procedures at three tiers

Materials

**Tier 1 – Initial
Technology
Development**

- Classical materials/system optimization research activities
- At home institution

**Structures and
Combinations**

**Tier 2 – Key
Advancement
Characterization**

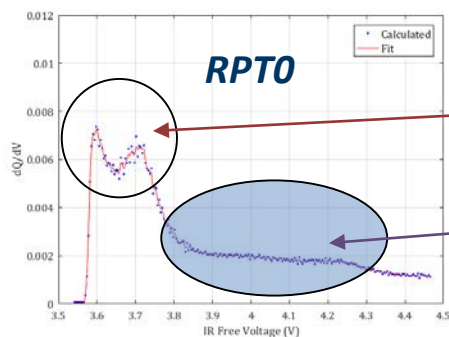
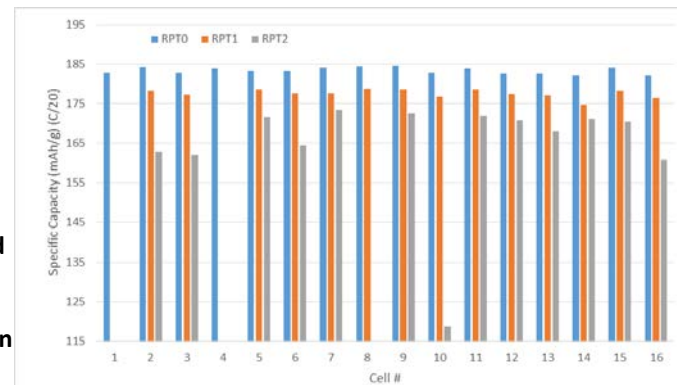
- Optimized plans to minimize impact to equipment/human resources

Full Cells

**Tier 3 - Cross
Program
Comparison and
Gap Analysis**

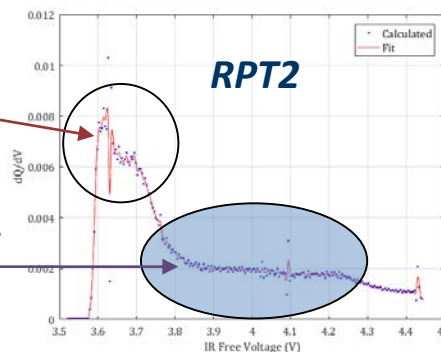
- Increased depth and length
- Direct interactions with characterization efforts
- At INL

Fade over first 50 cycles



Non-uniform particle performance/polarization

Little overall fade in cathode performance



**Implications to life,
performance and
thick electrode
design**

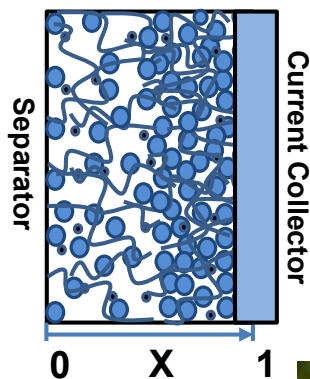
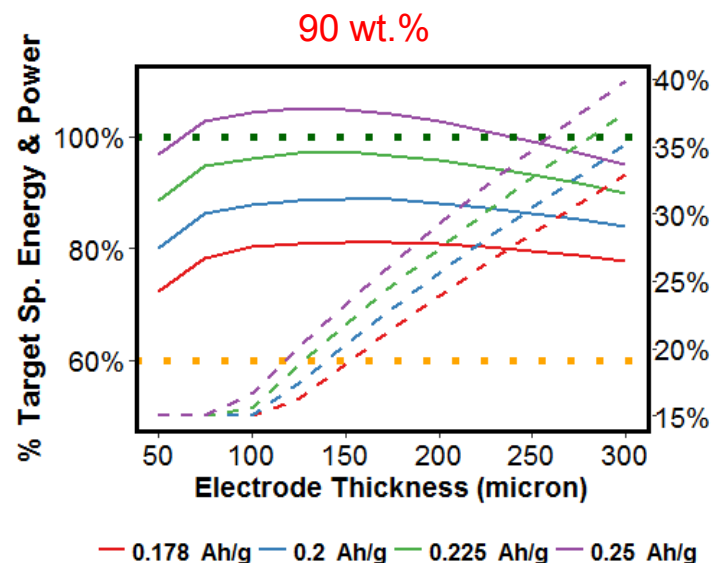
Responses to Previous Year Reviewers' Comments

- This project is a new start.

Remaining Challenges and Barriers

- Achieving dendrite free Li deposition with more than 99.9% coulombic efficiency.
- Increasing structural stability to over 4.5 volts.
- Increasing stability window of electrolytes and interfacial stability on both cathodes and anodes.
- Developing thick electrode architectures.
- Optimizing materials properties on the cell level.

Analysis on Li/C||NMC622 system



- At 90 wt%, 500 Wh/kg met at 225 mAh/g for electrodes in the 75-150 micron range and porosity in the 15 to 25% range.
- α important for NMC-Li – electrode architecture is key
 - High α requires greater porosity for same thickness to keep ohmic resistance from dominating.



Proposed Future Research

- Integrate the multi-institute capabilities in battery materials and chemistry, electrode architecture, cell design and fabrication, and advanced diagnosis to maximize materials utilization and optimize the materials performance in realistic cell architectures.
- Focus on three keystone projects:
 - 1) *Materials and Interfaces* – High utilization of high-energy cathodes and high-capacity Li metal anode by developing interface doping/coating on cathode materials and novel electrolyte for stable operation of Li metal anode.
 - 2) *Electrode Architecture* – New electrode architectures to increase electrode thickness and maximize active materials utilization, and 3D Li architectures to stabilize the metal anode.
 - 3) *Cell Design and Integration* – A new battery design to decouple cathode and anode interfacial reactions to achieve more than 500 Wh/kg energy density, and standard methodology to perform diagnostic evaluation and performance validation of the battery.

Any proposed future work is subject to change based on funding levels.

Summary

- ✓ Established the criteria to achieve the 500 Wh/kg goal for both high Ni NMC and sulfur systems.
- ✓ Demonstrated progress on the Keystone Projects:
 - Developed synthetic approaches, doping methods and surface coatings to stabilize high Ni NMC cathodes exhibiting ~220 mAh/g with superior cyclability, rate capability, and power density compared to the control cell.
 - Developed several electrolytes with greatly improved stability towards both NMC cathode and Li metal anode with Coulombic efficiency higher than 98%.
 - Developed new concepts on self-healing polymers and ordered architectures to control lithium metal deposition.
 - Developed new perovskite solid state electrolytes with good Li ion conductivity.
 - Demonstrated good progress on electrode architectures and full cell performance.

Acknowledgements

- Support from the DOE Vehicle Technologies Office Battery500 Consortium through Advanced Battery Materials Research Program is greatly appreciated.

Technical Backup Slides

Approach based on three Keystone Projects

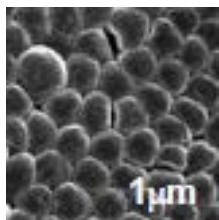
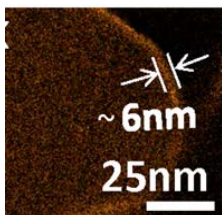
Extract Maximum Capacity from Promising Battery Chemistries

High Ni NMC-Li: achieving >50% of theoretical capacity at cell level

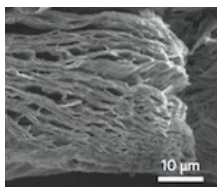
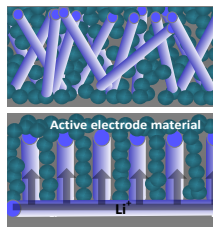
Solid State Li-S: solving polysulfide dissolution and Li degradation problems

Diagnosis & prognosis, assessment and validation

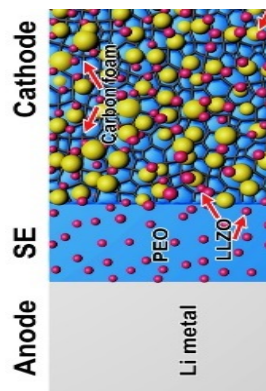
1. Materials/Interfaces:
Mixed conductive coating
Controlled surface reaction



2. Electrode Architecture
Thick, conductive cathode
3D Li composite structure



3. Cell Design/Integration
Cell modeling
1D or 2D Li conductor
De-coupled SEI reactions



Technology off
ramp to improve
Li ion batteries

Li batteries
500 Wh/kg
1000 cycles

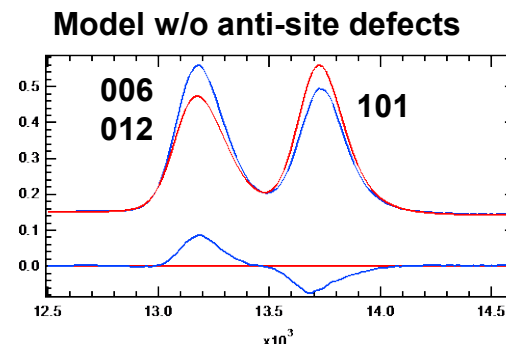
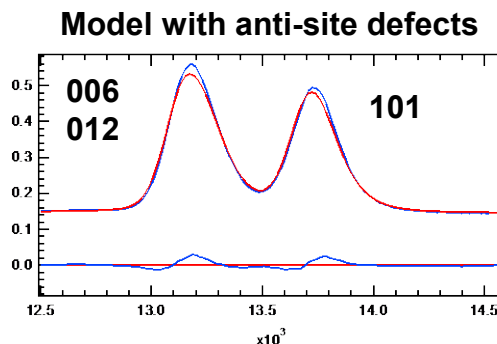
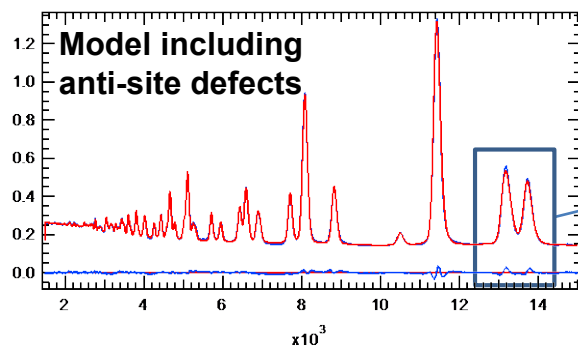
New test bed or
spin-off to scale up
technologies in US

Seedling projects: emerging concepts, alternative cathodes, 3D printed architectures, layer-by-layer fabrication of solid electrolytes, etc.

Technical Accomplishments

Neutron diffraction studies of NMC cathodes

- Neutron diffraction carried out at ORNL SNS
 - Work done under Programmatic proposal for Battery500
 - **Only the 2nd awarded Programmatic proposal in history of facility**

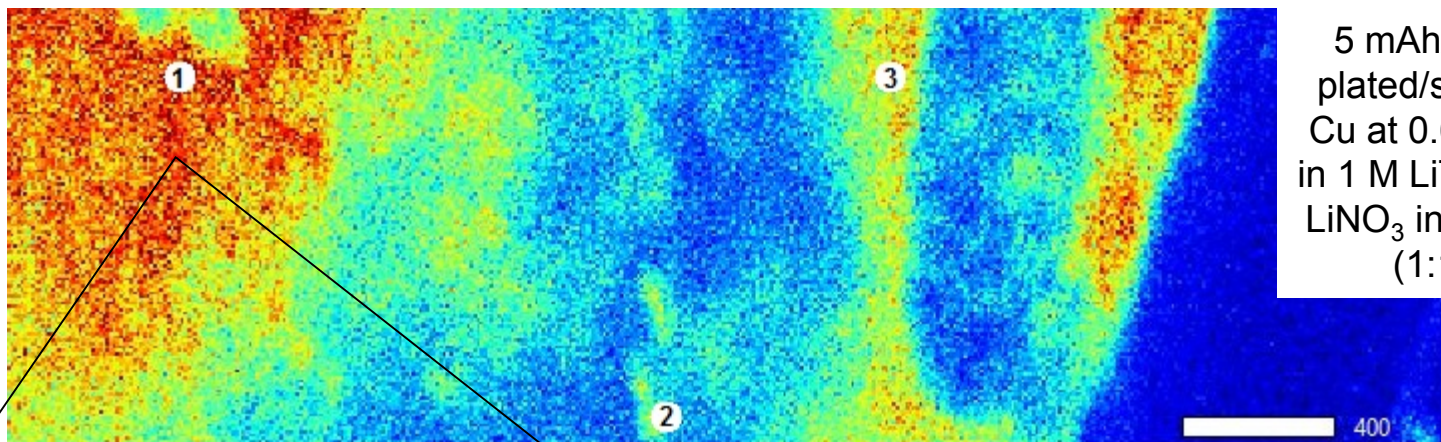


- ▶ Refinement is very sensitive to non-stoichiometry and defects
 - Most sensitive in vicinity of 006, 012, and 101 peaks
 - Anti-site defects could be resolved at the level of 0.1% (absolute)
 - Also sensitive to variations in TM stoichiometry on 1% (absolute) level
- ▶ Diffraction studies will allow influence of synthesis method on performance - influencing structural defects to be sensitively and directly resolved

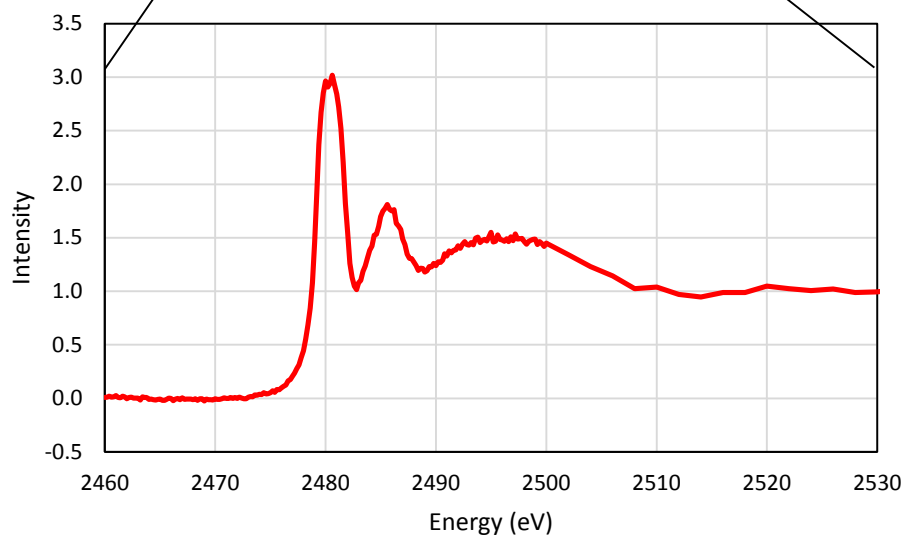
Technical Accomplishments

μ XAS Mapping of SEI on Li and Cu

Develop spectro-microscopy to map SEI on Li

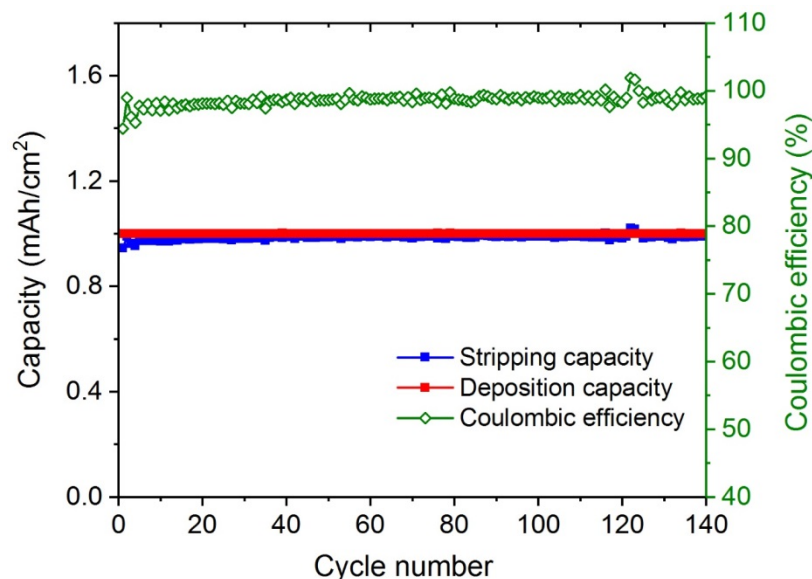
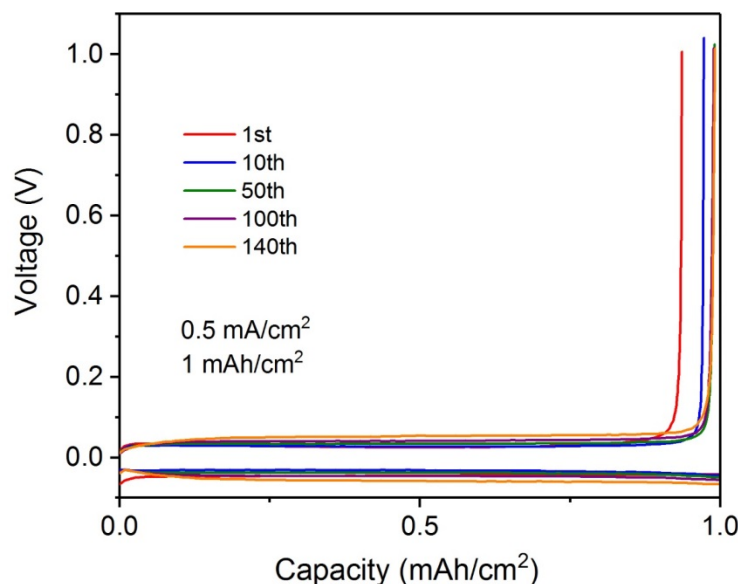


5 mAh/cm² of Li
plated/stripped on
Cu at 0.65 mA/cm²
in 1 M LiTFSI, 0.3 M
LiNO₃ in DOL/DME
(1:1, v/v)



Technical Accomplishments

Coulombic efficiency and cell performance of high concentration electrolyte E2 in Li metal battery



- Li||Cu cells with 75 μ L electrolyte.
- Cycling under deposition of 1 mAh/cm² and stripping to 1.0 V at 0.5 mA/cm² current density.
- ✓ High concentration E2 electrolyte has an average CE of 98.6% in Li||Cu cells.
- ✓ This electrolyte shows very good compatibility and stability with Li metal anode.



Technical Accomplishments

Graded electrode: Approach and simulation

